

Characterization of salt hydrates for compact seasonal thermochemical storage

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ABSTRACT

The salt hydrates $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, $\text{Al}_2\text{SO}_4 \cdot 18\text{H}_2\text{O}$, $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ and $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ were studied as possible thermochemical materials for seasonal heat storage of solar heat. It is possible for all four salt hydrates to be dehydrated at temperatures that can be achieved with a medium temperature collector. Based on temperature lifts observed during hydration, it was found that operating at low pressure significantly improves the vapor transport in the system in comparison to atmospheric pressure hydration. The observed temperature lift realized during hydration was found to be dependent on the type of salt: under identical conditions, the chlorides ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ and $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$) achieved a significant larger temperature lift than the sulfates ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ and $\text{Al}_2\text{SO}_4 \cdot 18\text{H}_2\text{O}$). However, the chlorides tend to form a gel-like substance due to melting or the formation of a solution.

1. BACKGROUND

In the Netherlands a large part of the domestic primary energy consumption (~65%) is used for space heating and domestic hot water preparation (Opstelten et al, 2007). This heat demand can be reduced by energy saving measures (improved insulation, heat recovery, and so on). A substantial part of the remaining heat demand can be fulfilled by using renewable energy sources such as solar energy.

The heat demand during the summer can be completely covered using solar heat, but in winter the heat demand exceeds the solar supply. To accommodate this difference in time between the solar energy surplus in summer and the energy demand in winter, a seasonal thermal storage is needed. Traditionally, water is used for storing solar heat (e.g. solar boiler) for short time periods. However, long-term heat storage requires a large water tank (>25-50 m³) that is often too large to be placed inside a building. A more compact way of storing heat is by means of thermochemical materials (TCM). The theoretical energy densities of these TCMs are several times larger than water. The basic reaction process for thermal energy storage using TCMs is: $\text{C (solid)} + \text{Q (heat)} \Leftrightarrow \text{A (liquid/gas)} + \text{B (solid)}$

During the summer, the thermochemical material (solid C) separates into the liquid or gas A and the solid B by adding heat from a solar collector. Materials A and B can be stored separately until a later time. In winter, A and B are mixed to start the reverse reaction to release the stored solar heat. No reactions occur as long as the two components (A and B) are stored separately, which means that thermochemical storage can be used for loss-free storage and transportation of heat. This is particularly advantageous when TCMs are used for long-term heat storage. Interesting TCMs are cheap, non-toxic, non-corrosive, have sufficient energy storage density and have reaction temperatures in the proper range. These requirements are fulfilled by a large number of salt hydrates by means of the following reaction: $\text{Salt} \cdot n\text{H}_2\text{O(s)} + \text{heat} \Leftrightarrow \text{Salt(s)} + n\text{H}_2\text{O(g)}$

A theoretical study at ECN identified four salt hydrates as most promising materials for compact seasonal heat storage: $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, $\text{Al}_2\text{SO}_4 \cdot 18\text{H}_2\text{O}$, $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ and $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$. In a previous study at ECN, the use of $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ as TCM for compact seasonal heat storage was investigated (van Essen et al, 2009). Detailed experiments on a milligram scale at

atmospheric pressure revealed that the material was able to take up and release almost 10 times more energy than a water storage of the same volume. It was also found that the hydration of MgSO_4 proceeds quite slowly (5-20 hours) which limits a fast and full release of the stored solar heat, especially for a thick layer of material. Additionally, the material is not able to take up water above 40°C as would be required for space heating and domestic hot water preparation. This means that the water uptake of the material has to be improved in order to be applied for compact seasonal heat storage. A possible solution is to perform the hydration experiments at low pressure in order to remove the inert gasses present in the system and to reduce the pressure drop between the water and the salt (Zondag et al, 2008). For this reason the potential of the selected four salt hydrates as TCM for compact seasonal heat storage was investigated under low pressure conditions. In this paper, the results of these measurements are presented with the focus on the hydration experiments.

2. EXPERIMENTAL METHOD

2.1. DEHYDRATION EXPERIMENTS

In a TCM heat storage system, a medium temperature collector (vacuum tube) is used to dehydrate the salt hydrate. In this paper it is assumed that these collectors deliver heat at a maximum temperature of 150°C . During the dehydration experiments, an oven was used to heat up 40 gram of salt hydrate at atmospheric pressure from room temperature to 150°C . In previous experiments using $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, it was found that melting occurred when the heating rate was higher than $1^\circ\text{C}/\text{min}$ (van Essen et al, 2009). Therefore it was decided to keep the heating rate constant at $1^\circ\text{C}/\text{min}$ during the dehydration experiments.

Thermogravimetric analysis (TGA) was used to obtain more detailed information on the dehydration reactions of the four salt hydrates. TGA involves the measurement of the mass change as function of time subjected to a predefined temperature program using the same heating rate as for the oven experiments. The TGA measurements were performed at atmospheric pressure since the apparatus was not capable of performing experiments at sub-atmospheric pressures.

2.2. HYDRATION EXPERIMENTS

A closed fixed bed hydration-dehydration setup was designed and constructed to test the hydration behavior of salts. This experimental setup is shown in Figure 1:

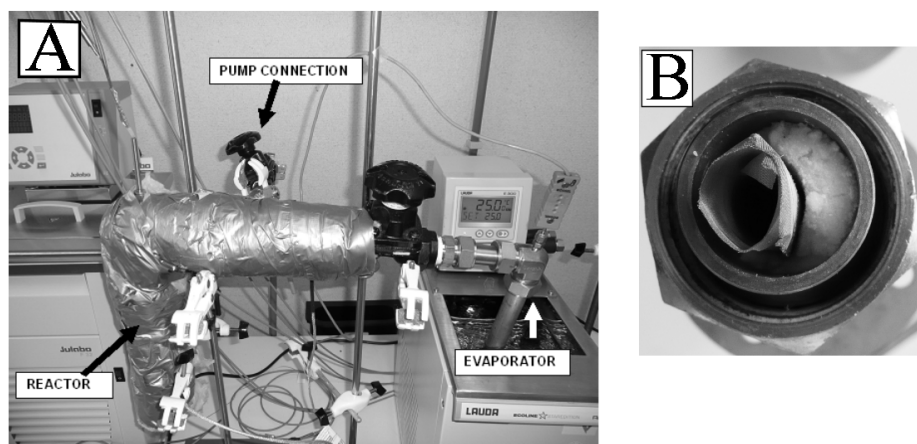


Figure 1. **A.** Schematic overview of experimental setup for analyzing the four salt hydrates, **B.** Top view of fixed bed reactor

The experimental setup consists of a fixed bed reactor (left part in Figure 1A) with a storage volume of 98 ml. In the centre of the reactor a cylindrical metal mesh with aperture size of 40 μ m is placed that acts as a vapor channel to facilitate the water transport to the salt during hydration (see also Figure 1B). The reactor is filled with approximately 40 grams of dehydrated salt from the oven. The fixed bed reactor is connected to an evaporator and a vacuum pump system. The evaporator (right part in Figure 1A) is made of stainless steel and is immersed in a thermostat bath filled with water to control the temperature inside the evaporator. The vacuum pump system consists of a pressure sensor and two diaphragm vacuum pumps connected in series to evacuate the system to low pressure (2.8 mbar). Six K type thermocouples were placed inside the fixed bed reactor and one K type thermocouple was placed in the evaporator/condenser to monitor the temperature during the experiments. The data from the thermocouples were digitized using a data acquisition unit and stored on a PC. The hydration experiments for all salts were performed under two conditions:

	Reactor	Evaporator	
	Temperature ($^{\circ}$ C)	Temperature ($^{\circ}$ C)	Water vapor pressure (kPa)
I	25	25	3.2
II	50	10	1.3

Table 1: Experimental conditions during hydration experiments

In a previous study it was found that MgSO₄ did take up water while releasing heat at 25 $^{\circ}$ C. Therefore, it was decided to keep both reactor and evaporator temperature at 25 $^{\circ}$ C in the first hydration experiments. However, under practical conditions, the water vapor is supplied by an evaporator connected to a borehole heat exchanger at 10 $^{\circ}$ C, which corresponds to a saturation water vapor pressure of 1.3 kPa. The heat released during the hydration reaction is used for e.g. space heating. A typical domestic heating system requires temperatures above 40 $^{\circ}$ C. To study the hydration under practical conditions, a heating cable was placed around the fixed bed reactor which kept the reactor at a constant temperature of 50 $^{\circ}$ C. In this way, the hydration behavior of the four salts can be studied under more realistic conditions

3. EXPERIMENTAL RESULTS

3.1. MAGNESIUM SULFATE (MgSO₄·7H₂O)

Dehydration of a sample of MgSO₄·7H₂O in the oven resulted in a mass loss of 42.2 %. This mass loss corresponds to the value found at 150 $^{\circ}$ C in a previous study (van Essen et al, 2009) and corresponds to the following reaction:



It means that the starting product of the hydration experiments is MgSO₄·H₂O (Kieserite), which is a known stable species in the magnesium sulfate-water system. The result of the hydration experiments is shown in Figure 2, where the maximum temperature difference (ΔT) is plotted as function of the time:

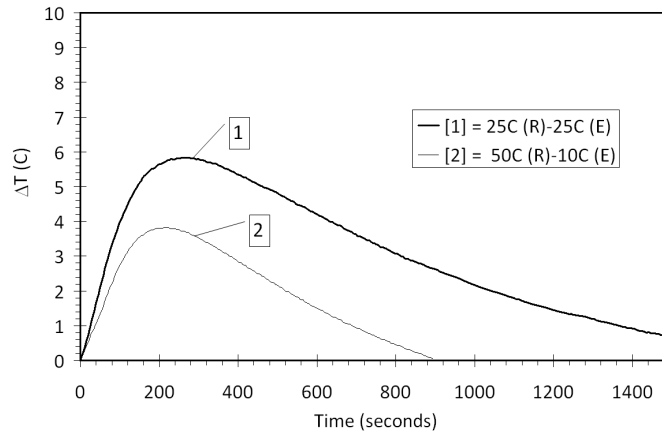


Figure 2: Temperature profile for the hydration of $\text{MgSO}_4 \cdot \text{H}_2\text{O}$ at low pressure under two different conditions (see also Table 1). ‘R’ denotes the reactor and ‘E’ the evaporator.

The experimental results acquired at 25°C (both reactor and evaporator) confirm the observation from the previous study that the material is able to release heat at 25°C . At low pressure and under practical conditions, $50\text{C}(\text{R})-10\text{C}(\text{E})$ in Figure 2, the hydration results in a small but noticeable temperature lift of 4°C as a result of water taken up by the material. This result is surprising since the material was unable to take up water and release heat in previous experiments performed at atmospheric pressure (van Essen et al, 2009). It seems that operating at reduced pressure improves the water vapor transport to the dehydrated material. The result indicates that a closed TCM heat storage system operating under low-pressure is preferred above an open system.

3.2. ALUMINUM SULFATE ($\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$)

The TGA curves for the dehydration of aluminum sulfate performed in dry nitrogen atmosphere is shown in Figure 3:

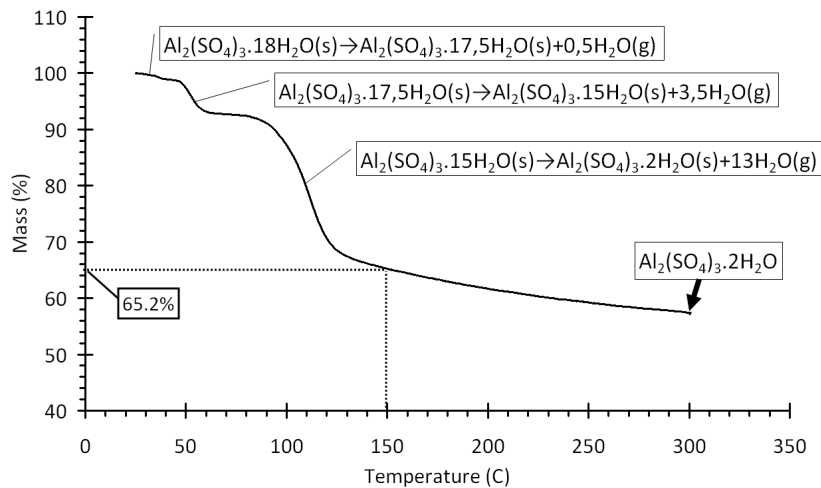
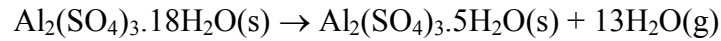


Figure 3: Mass (TGA) as function of temperature for dehydration of $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$. The dehydration was performed by heating a sample of 10 mg from 25°C to 300°C with $1^\circ\text{C}/\text{min}$ in a dry nitrogen atmosphere.

The TGA results indicate that the material is dehydrated in three discrete steps as shown in the above Figure, but that the material is not even completely dehydrated at 300°C . However, at

150°C a mass loss of $100-65.2=34.8\%$ can be expected that corresponds to expelling 13 water molecules:



Dehydration of the material using the oven resulted in a mass loss of 34.7%, which is in excellent agreement with the TGA result. Figure 4 shows the result of the hydration experiments performed at low-pressure:

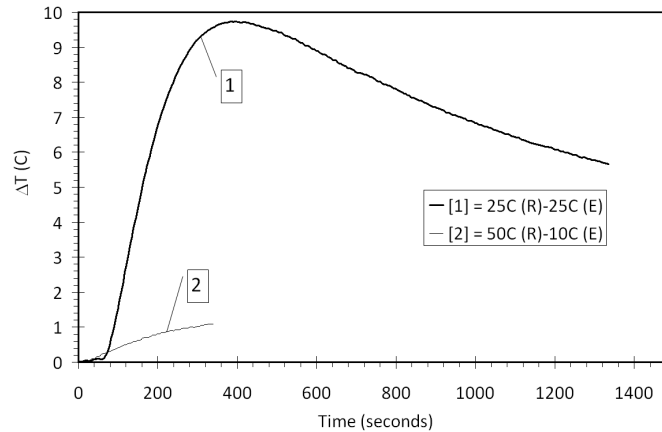


Figure 4: Temperature profile for the hydration of $\text{Al}_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$ at low pressure under two different conditions (see also Table 1). ‘R’ denotes the reactor and ‘E’ the evaporator.

The result obtained at a reactor and evaporator temperature of 25°C shows a similar temperature lift ($\Delta T=10^\circ\text{C}$) as was found when using $\text{MgSO}_4 \cdot \text{H}_2\text{O}$ ($\Delta T=6^\circ\text{C}$, see Figure 6). The results for the experiment performed under practical conditions show a maximum temperature lift of 1-2°C, which is also quite similar to the value found for hydration of $\text{MgSO}_4 \cdot \text{H}_2\text{O}$.

3.3. CALCIUM CHLORIDE ($\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$)

The dehydration TGA curve for $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ is shown in Figure 5:

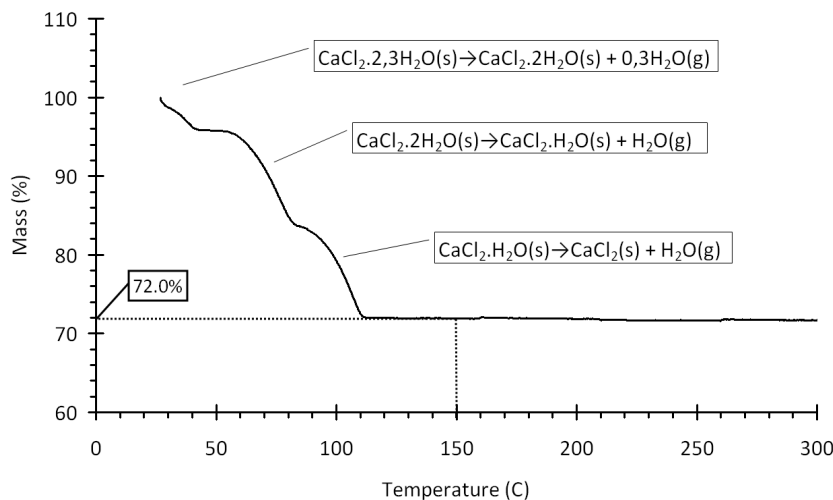
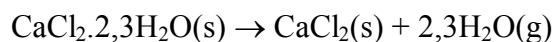


Figure 5: Mass (TGA) as function of temperature for dehydration of $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$. The dehydration was performed by heating a sample of 10 mg from 25°C to 300°C with 1°C/min in a dry nitrogen atmosphere.

Based on the mass loss from the TGA curve, it was discovered that the starting material is $\text{CaCl}_2 \cdot 2,3\text{H}_2\text{O}$ instead of $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$. This result is not unexpected since calcium chloride is a hygroscopic salt and already takes up water at room temperature. As can be seen in Figure 5, a mass loss of $100-72=28\%$ is found at 150°C corresponding to the following reaction:



For the sample dehydrated in the oven a mass loss of 24.5% was observed, which is in good correspondence with result at 150°C from the TGA curve. The anhydrous calcium chloride from the oven was further investigated on the hydration behavior at low pressure. The results of these experiments are shown in Figure 6:

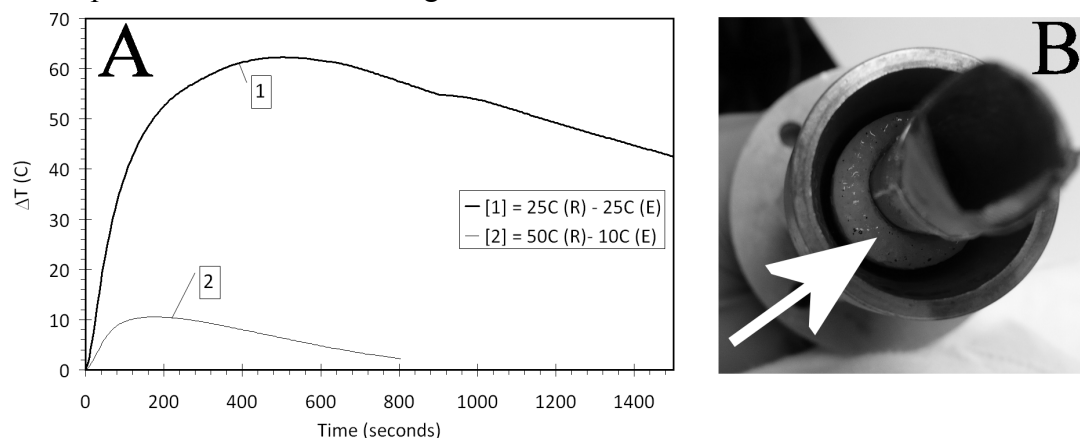


Figure 6: **A.** Temperature profile for the hydration of CaCl_2 at low pressure under two different conditions (see also Table 1). ‘R’ denotes the reactor and ‘E’ the evaporator, **B.** Calcium chloride sample (indicated by the white arrow) after hydration.

The results show that the behavior of calcium chloride is quite different from the behavior of the two sulfates (see above) since considerable larger temperature lifts can be achieved using calcium chloride: a maximum $\Delta T=62^\circ\text{C}$ for a reactor and evaporator temperature of 25°C and maximum $\Delta T=11^\circ\text{C}$ under practical conditions. However, after the dehydration the material appeared to be a gel probably due to melting of the material or the partial formation of a solution of this hygroscopic salt (Zondag et al, 2008). This is an undesired effect since it reduces the bed porosity of the material and the ability of the material to hydrate again.

3.4. MAGNESIUM CHLORIDE ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$)

The TGA dehydration curve for $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ is shown in Figure 7.

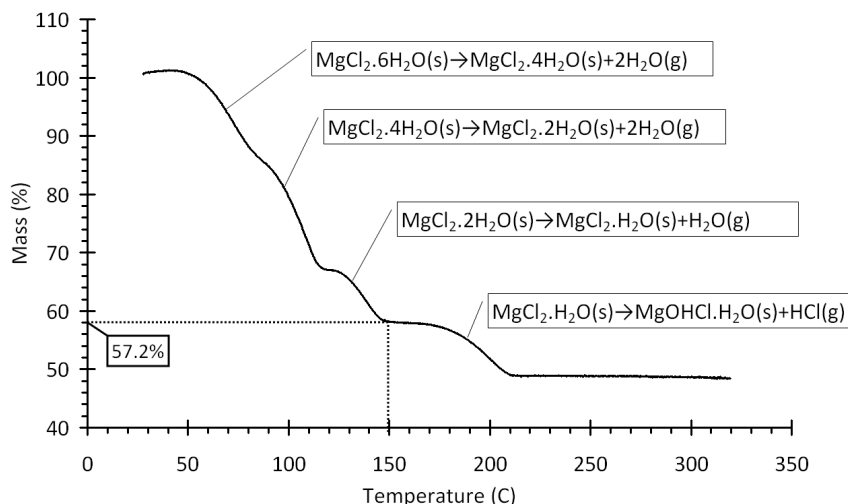


Figure 7: Mass (TGA) as function of temperature for dehydration of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$. The dehydration was performed by heating a sample of 10 mg from 25°C to 300°C with $1^\circ\text{C}/\text{min}$ in a dry nitrogen atmosphere.

As can be seen in the above Figure, at 150°C a mass loss of $100 - 57.2 = 42.8\%$ is observed, which corresponds to the following reaction:



A sample that was dehydrated in the oven, showed a smaller mass loss of 37.8% corresponding to the formation of $\text{MgCl}_2 \cdot 2\text{H}_2\text{O}$:



The difference between the mass losses (42.8% vs. 37.8%) is very small and it could be caused by a small experimental error (e.g. during weighting the sample). Nevertheless, since the sample from the oven is used for hydration experiments, it was assumed that the starting material is $\text{MgCl}_2 \cdot 2\text{H}_2\text{O}$. The results of the hydration measurements are shown in Figure 8:

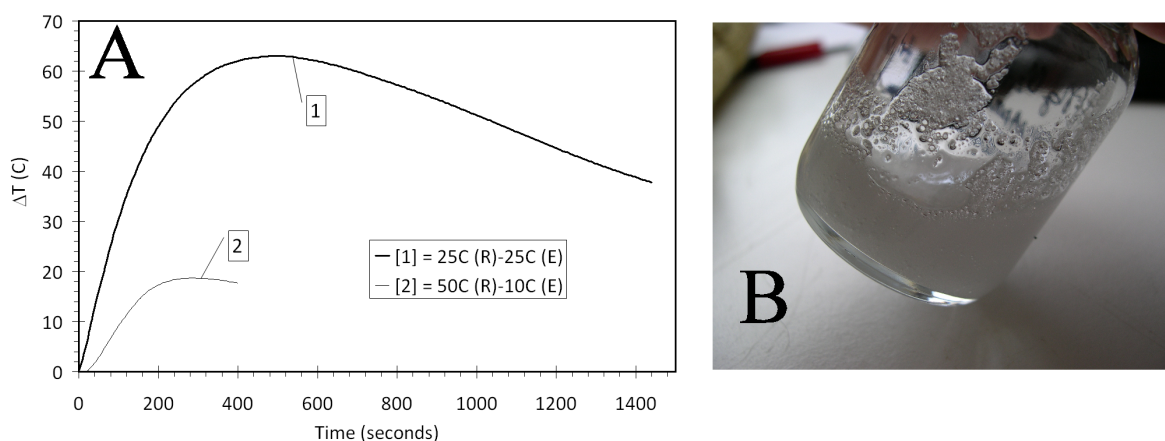


Figure 8: **A.** Temperature profile for the hydration of $\text{MgCl}_2 \cdot 2\text{H}_2\text{O}$ at low pressure under two different conditions (see also Table 1). ‘R’ denotes the reactor and ‘E’ the evaporator, **B.** Magnesium chloride sample after hydration to ambient air at atmospheric pressure.

The temperature lift for a reactor and evaporator temperature of 25°C is comparable to the one found for calcium chloride: $\Delta T = 63^\circ\text{C}$. However, when the material is hydrated under practical conditions a temperature lift of 19°C was found: the largest temperature lift that was found for

the four salt hydrates under investigation. After dehydration a gel was formed, similar to the one observed after the calcium chloride hydration experiment. Here too, the gel-like structure of the material can be the result of melting or the formation of a magnesium chloride-water solution. This gel-like substance was also observed when the dehydrated material was exposed to ambient air at room temperature as can be seen in Figure 8B.

3.5. PRACTICAL CONSIDERATIONS

In a TCM heat storage system, the heat generated during the hydration is transferred to e.g. a space heating systems by means of a heat exchanger. Due to a temperature loss over the heat exchangers, it can be expected that the sulfates (magnesium sulfate and aluminum sulfate) are less suitable as TCM due to the small temperature lifts. On the other hand, under practical conditions the chlorides (magnesium chloride and calcium chloride) show large temperature lifts ($\Delta T=11-19^{\circ}\text{C}$) which means that heat at a higher temperature can be delivered to the residential heating system. A disadvantage of the chlorides is that these materials melt or form solutions after exposure to water vapor (see above).

4. CONCLUSIONS

It was found that $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$, $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ and $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ can be dehydrated at 150°C , a temperature that can be reached by a medium temperature collector (vacuum tube). Hydration experiments performed in a newly constructed setup suggest that operating at low-pressure improves water vapor transport in the system. The results indicate that a closed low-pressure TCM heat storage system is required for the successful application of salt hydrates. The hydration experiments also show that the chlorides (magnesium chloride and calcium chloride) show a larger temperature lift than the two sulfates (magnesium sulfate and aluminum sulfate). However, the hygroscopic chlorides tend to form a gel-like material, which is due to the melting of the material during hydration or the formation of a solution.

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